Biointerface Research in Applied Chemistry
Open-Access Journal (ISSN: 2069-5837)

Article
Volume 13, Issue 6, 2023, 570
https://doi.org/10.33263/BRIAC136.570

Adsorption and Kinetic Studies of Polyacrylamide (PAA) Hydrogels for Efficient Removal of Methylene Blue (MB) in Aqueous Media

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Scopus Author ID 57214875106
Received: 14.11.2022; Accepted: 6.01.2023; Published: 19.03.2023

Abstract: In this study, the removal of methylene blue dye was investigated in aqueous media using polyacrylamide (PAA) through a series of batch assay methods. The parameters of the batch assay were selected with respect to contact time, temperature, and pH of the medium. The optimized adsorption conditions for MB dye removal using PAA were found to be 1024 mg g^{-1} at pH 8.8 at 120 min contact time and 25 °C temperature. As a Langmuir isotherm model was found suitably well-fitted over the Freundlich model, suggesting that the reaction favors the pseudo-second-order kinetics with endothermic nature. According to the study's findings PAA, hydrogels are useful materials in aqueous solution for removing MB dye which can be commercialized through proper channels.

Keywords: organic dyes; wastewater; polyacrylamide; adsorption; kinetics.

1. Introduction

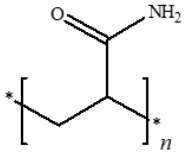
Fresh water is not a primary need of humans and wildlife on the earth but is also an essential segment for maintaining a healthier life. The worldwide threat of increasing pollution is gaining much attention amongst the scientific community, leading to water scarcity and water pollution. Day by day, various contaminants/pollutants (inorganics-heavy metal ions or organics-dyes) have been added into our water ecosystem by the intensive industrialization and urbanization activities involving a large number of industry bodies, chiefly, textiles & clothing, battery, distilling, mining, metallurgy, electroplating, etc. [1-3]. However, several metals are essential to various biochemical processes in our daily life. But, the presence of heavy metals/ions and several organic dyes in the water system cope with severely harmful and many adverse responses because of their highly toxic nature with high stability and non-biodegradability [4-7].

The most common industrial effluents contain high-density metal ions (~5 g cm^{-3}) with highly stable as well as acutely toxic oxidation states, including Hg(II), Cd(II), Pb(II), Cr(VI),

Zn(II), Cu(II), Ni(II) and a large number of organic dyes, especially azo dyes are big being considered globally as a most challenging environmental concern [5-10]. Therefore, a pressing global demand has emerged for removing toxic metals and organic dyes from wastewater at the acquittal stage to make the aquatic environment safer. So far, various methodologies have been developed and utilized to remove contaminants from wastewater, including solvent extraction, oxidation-reduction, electrophoresis, precipitation, reverse osmosis, electrolysis, adsorption, ion exchange, coagulation and membrane separation are all examples of processes. [3, 8-10]. Amongst the existing methods, adsorption is a recognized and broadly accepted method due to its cost-effectiveness and easy handling, with significant efficacy in adsorbing heavy metal ions from wastewater [11-15]. However, many adsorbents have been developed and utilized to remove organic dyes, and harmful heavy metal ions, such as alumina and metallic and metal oxide nanoparticles [14, 15], but few limitations were observed, including adsorption efficiency, reusability, and commercialization.

In the present scenario, great interest in wastewater treatment emerged with new adsorbent development capped with superior properties over conventional ones, such as stability, low cost, and high adsorption efficiency at a fast rate. Several polymeric functionalized materials showed great attentiveness due to their adsorption efficiencies towards many toxic ions as well as organic dyes [16, 17]. In this regard, smart adsorbents based on cleaner synthetic routes are being considered, such as activated carbon, zeolites, biomass wastes, nanoclay, composite polymers, and metal-free and metal-containing organic frameworks [18-21].

Polyacrylamide (Scheme 1), a 3D network material with large numbers of amide side groups, has excellent water-swollen as well as regeneration abilities. PAA has been effectively implanted as specific sorbents to remove environmental pollutants like dyes and heavy metal ions in aqueous solutions [22-24]. Consequently, in the present work, PAA was explored to assess adsorption efficiency as an adsorbent for MB dye in aqueous media.



Scheme 1. Chemical structure of PAA.

2. Materials and Methods

2.1. Materials and equipment.

All chemicals and reagents were of analytical grade and utilised without additional purification. Methyl blue was procured from Sigma-Aldrich, and PAA (Molecular weight = ~12000) and other consumables were from Qualigens. The stock solution of MB was prepared by accurately weighing and dissolving it in double distilled water. All chemicals and reagents were used without further purification. Lambda 800/900 Perkin Elmer Spectrophotometer was used for absorption studies in the ultra-violet and visible range.

2.2. Methods.

2.2.1. Activation of PAA.

PAA hydrogels were activated by immersing them in distilled water for 3 h until a state of swelling-equilibrium reached under occasional superficially wiping using a filter paper.

2.2.2. Preparation of aqueous media containing MB dye.

The stock solution was prepared by dissolving MB 1 g in 1 L double distilled water. Several desired concentrations were made by diluting this stock solution with water accordingly for further experiments (0.1 to 0.5 g L^{-1}).

2.2.3. Assessment of Adsorption efficiency for MB dye removal.

The batch assay method was employed to assess the adsorption behavior of PAA as an adsorbent. About 0.05 g of the adsorbent was added to 50 mL of 10 mg L^{-1} MB dye as adsorbate in aqueous media containing MB dye. The mixture was shaken using a mechanical shaker running at 100 rpm at ambient temperature (~25 ºC) for 5 min. In order to remove any adsorbent particles, an aliquot of the solution was then centrifuged at 2000 rpm (REMI) for 10 min, and the remaining dye concentration in the filtrate was measured at the maximum wavelength using a spectrophotometer. All of the experiments were duplicated for better precision. The adsorption efficiency of PAA for MB dye removal was evaluated in terms of various effects such as concentration (g L^{-1}), contact time (min), temperature (ºC), and media pH.

Using equation (1), the % removal of MB dye and the equilibrium adsorption capacity in the solid phase, q_e (mg g^{-1}), was assessed, and the % removal of dye was measured by the given equation (2):

$$q_e = (C_o - C_e)\frac{V}{w} \quad (1)$$

$$\%\ \text{Dye removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where C_o is the initial concentration (mg L^{-1}), C_e is the equilibrium concentration (mg L^{-1}), V is the volume of the solution (L), and w is the mass of the adsorbent.

C_e/q_e versus C_e was measured using the linear equation (3) [25]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (3)$$

2.2.4. Regeneration studies.

The regeneration studies for adsorption and desorption were carried out to assess the performance of regeneration after multiple cycles for adsorption and desorption.

3. Results and Discussion

3.1. Effect of contact time.

The influence rate of contact duration is seen in Figure 1 for the % removal of MB dye was assessed, and kept the initial concentration (50, 100, 200, 300 mg L^{-1}) at pH 6. It was observed from the figure that the maximum dye removal is reached at about 120 min flocculate-duration, and thereafter no noticeable removal was seen. However, the rate of dye removal is found to be higher initially may be on account of the adsorbent's unoccupied surface area.

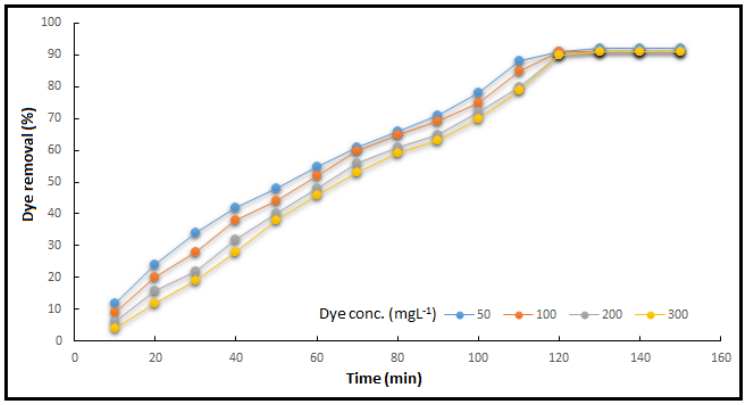


Figure 1. Effect of contact time. Time = 10-150 min; Dye concentration = 50, 100, 200, 300 mg L^{1}.

3.2. Effect of temperature.

The effect of temperature against the adsorption of MB dye was performed with respect to six variable ranges 10, 15, 20, 25, 30, 40, and 50 °C at pH 6. Figure 2 shows that the adsorption process is increased with an increase in temperature, possibly due to developing an enlargement outcome inside (internal molecules) of PAA feasible to the spear of MB dye molecules [26].

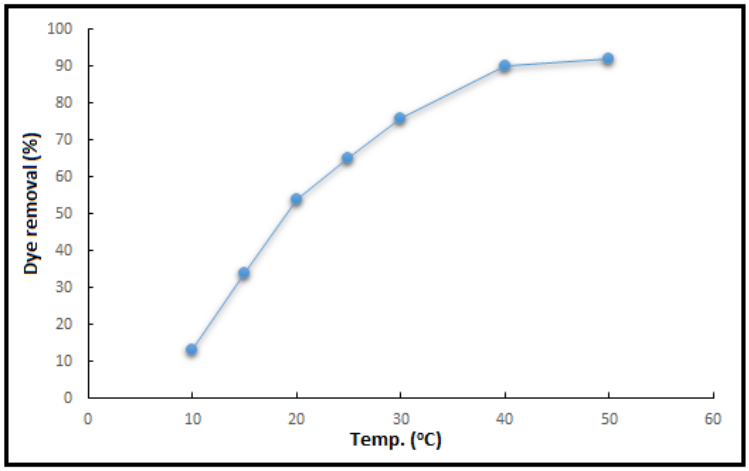


Figure 2. Effect of temperature at range = 10, 15, 20, 25, 30, 40, and 50 °C, pH = 6.

3.3. Effect of pH media.

Figure 3 represents the effect of pH media investigated to optimize the suitability of the highest adsorption using PAA with a pH range of 2–10 and 50 mg L^{-1} initial MB dye concentration

and adjusted using 0.1 mol L^{-1} HCl and NaOH. It was noticed from Figure 3 that an increase in pH value makes strong feasibility for higher dye adsorption, preferably between 8 and 10. The active sites are blocked with the formation of protonated species in lower pH, while at a higher pH range, the presence of much more ammonium moieties provides more sites for dye molecules to be absorbed.

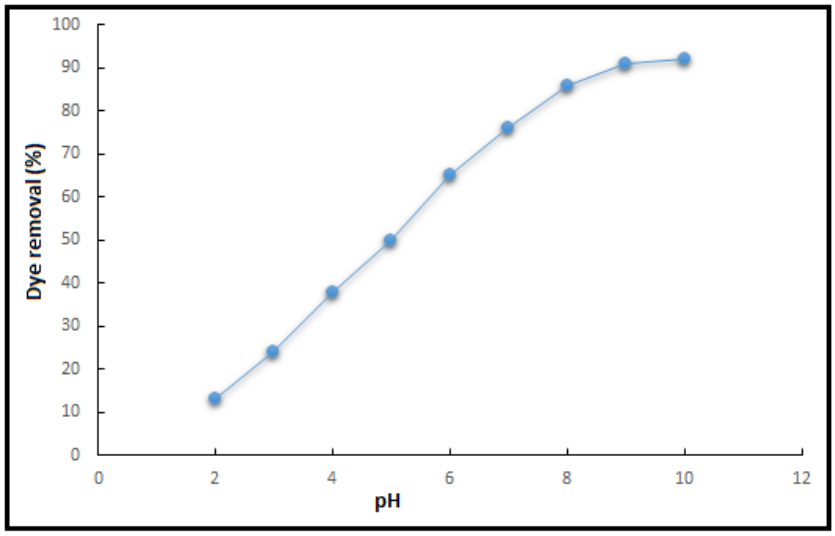


Figure 3. Effect of pH media, pH range = 2-10; initial MB dye concentration = 50 mg L^{-1}.

3.4. Adsorption isotherm results.

Langmuir and Freundlich isotherm models are considered for pseudo-first and pseudo-second order reactions to perform isotherm studies. Figure 4 shows the linear plots of C_e/q_e versus C_e corresponding to Langmuir isotherm at pH 5.8, which explains a suitable isotherm correlation with the adsorption process. Table 1 indicates the adsorption parameters. The constants can be assessed using the intercepts and the slopes. Figure 4 shows that Langmuir's isotherm suitably followed at equilibrium, indicating the homogeneous monolayer coverage of dye molecule on the outer surface of PAA resulted in identical activation energy. The separation factor, R_L entitles the type of isotherm defined in terms of equation (4):

$$R_L = \frac{1}{1+bC_0} \quad (4)$$

In the present study, the values of R_L is shown <1 (Table 1), indicating a satisfactory adsorption phenomenon of MB dye onto PAA hydrogels. For Freundlich isotherm, the values of K_f and *n* (Table 1) were calculated from the intercept and slope of the linear plots between *log* q_e vs. *log* C_e, respectively, and Freundlich equation (5) is stated as:

$$log\ q_e = log\ K_f + \frac{1}{n} ln\ C_e \quad (5)$$

The adsorption process is supposed to follow the Langmuir and Freundlich isotherms and occurs at certainly onto specific homogeneous sites inside the adsorbent molecules.

It was found that the Freundlich exponents, n greater than 1 indicate a favorable adsorption condition [27].

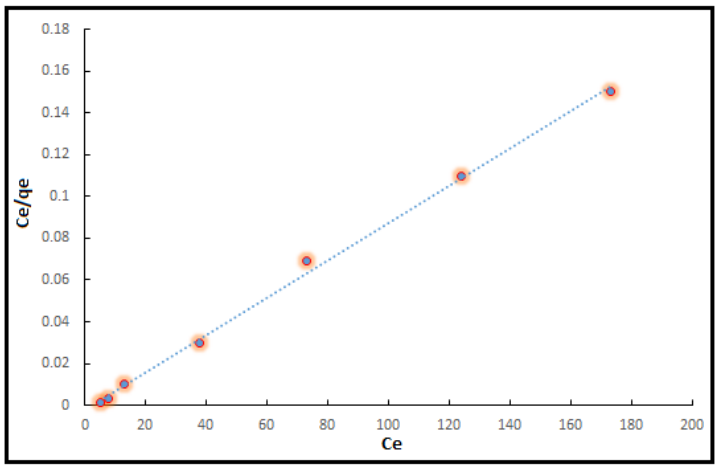


Figure 4. Langmuir plots for the adsorption of MB dye onto PAA.

3.5. Kinetics studies.

To recognize and understand the kinetics of the adsorption process, two well-known models, pseudo-first and pseudo-second-order models [28-30] were performed in terms of the order of rate constant, where K_1 and K_2 are the first-order and second-order rate constants (Table 2). The correlation coefficients were 0.982–0.997, which favors the pseudo-second-order kinetics (Figure 6). According to the experimental data, a pseudo-first-order rate equation was observed for MB dye removal.

3.6. Regeneration studies.

The regeneration studies for adsorption and desorption are given now in Figure 7 for three cycles. Some improvement is also added to the text now. Reuse is an important task for any adsorbent material that can perform satisfactory regeneration after multiple adsorption cycles. Figure 7 indicates a positive indication for PAA that can be utilized after many regenerated cycles.

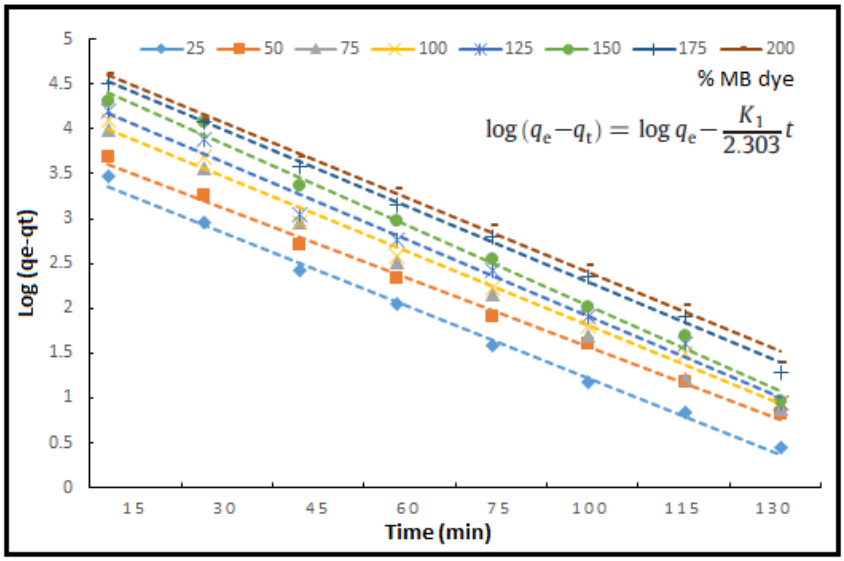


Figure 5. Pseudo-first-order kinetic plots for MB dye adsorption using PAA (Lagergren model, initial conditions t = 0 to t and qt =0 to qt).

Table 1. Parameters of Langmuir and Freundlich adsorption isotherm for the adsorption of MB dye onto PAA hydrogel.

Temp. (K)	Langmuir				Freundlich		
	q_{max} (mg g^{-1})	b (L mg^{-1})	R_L	R^2	K_f (mg^{1-n} L^n g^{-1})	*n*	R^2
298.15	1024	0.017	0.89	0.997	607	5.27	0.804

Table 2. Comparison of pseudo-first and pseudo-second order Kinetic models for MB dye adsorption onto PAA in aqueous media.

Dye conc. (mg L^{-1})	qe (exp.)	Pseudo-first order model			Pseudo-second order model		
		K_1 (g mg^{-1} min^{-1})	qe (Cal.)	R^2	K_2 (g mg^{-1} min^{-1})	qe (Cal.)	R^2
25	497	2.64×10^{-2}	343	0.981	3.64×10^{-5}	512	0.997
50	768	2.91×10^{-2}	671	0.984	4.04×10^{-5}	822	0.993
75	998	3.43×10^{-2}	785	0.997	5.37×10^{-5}	1092	0.992
100	1123	2.99×10^{-2}	1020	0.996	5.33×10^{-5}	1246	0.984
125	1264	3.62×10^{-2}	1308	0.989	4.76×10^{-5}	1423	0.997
150	1299	3.62×10^{-2}	1288	0.946	3.22×10^{-5}	1506	0.981
175	1356	3.66×10^{-2}	1198	0.964	3.98×10^{-5}	1586	0.983
200	1452	3.66×10^{-2}	1147	0.954	3.84×10^{-5}	1599	0.982

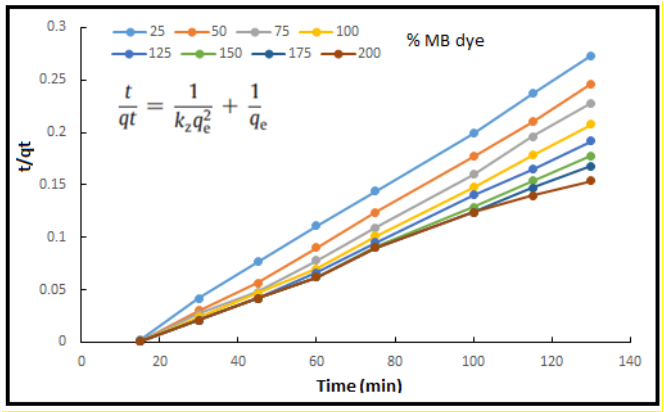


Figure 6. Pseudo-second-order kinetic plots for desorption onto polyacrylamide.

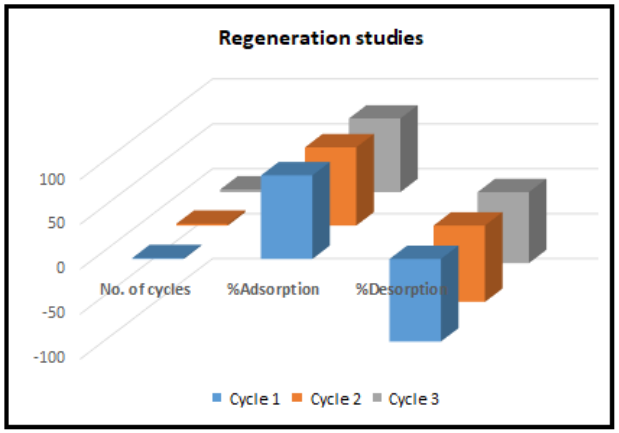


Figure 7. The regeneration studies for adsorption and desorption

4. Conclusions

In the present work, we use PAA to assess adsorption efficiency as an adsorbent for MB dye in aqueous media. The parameters of the batch assay were selected with respect to contact time, temperature, and pH of the medium. The optimized adsorption conditions for MB dye removal using PAA were found to be 1024 mg g^{-1} at pH 8.8 with 120 min contact time, and 25 °C temperature as a Langmuir isotherm model was found suitably well-fitted over the Freundlich model, suggesting that the reaction favors the pseudo-second-order kinetics. Results indicated that various functionally active sites provide feasibility to the high adsorption process and can be used at the commercial level to reduce wastewater pollution from organic dye contaminants. After several reuse cycles, remarked potential was also noticed. The presented adsorbent materials in this study can pave the way for future research with respect to the existing adsorption options, and after pilot scale projects may be utilized at the commercial level.

Funding

This research received no external funding.

Acknowledgments

Prof. P. K. Bharti, Vive-Chancellor, of Glocal University, is highly acknowledged for his suggestive and positive moral support.

Conflicts of Interest

The authors declare no conflict of interest.

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